Modelling the linear dynamics of Double Dynamics Polymer Networks

Introduction to Tube model

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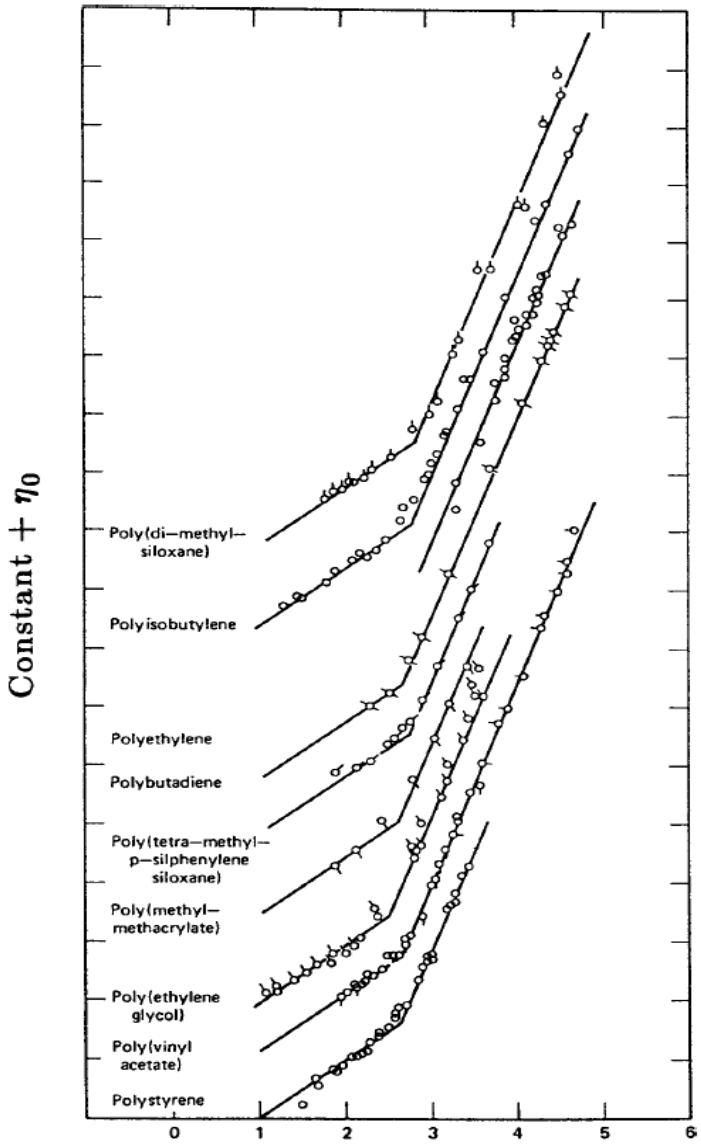
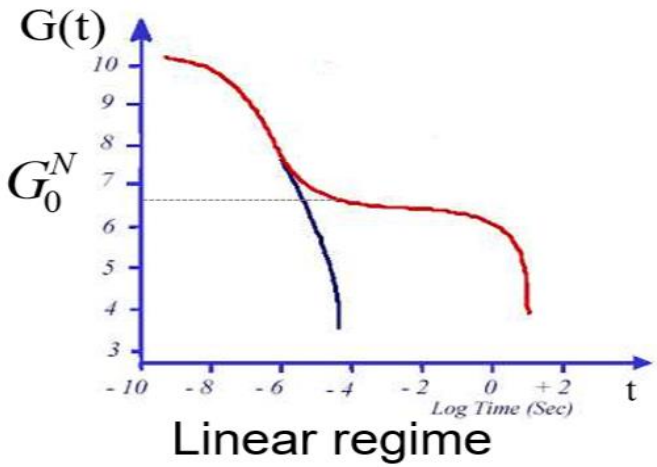
Molecular weight dependence of viscosity



Wide range of chemically and structurally different polymers display the same molecular weight dependence of viscosity. Abrupt change in the scaling exponent at a certain critical molecular weight.

$$\eta_0 \propto M^{\alpha} \begin{cases} M>M_c,\ \alpha=1 \\ M>M_c,\ \alpha \text{ close to } 3.2\text{-}3.4 \end{cases}$$



What is entanglement?

How they interpenetrate and entangle?

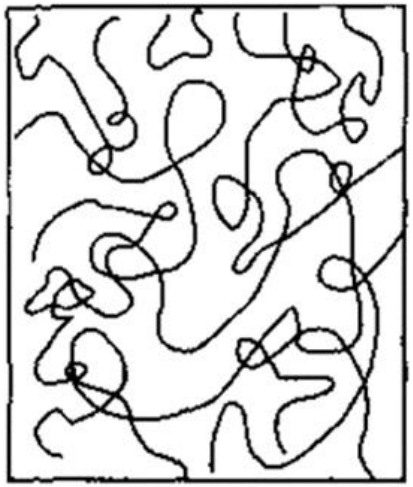
The molecular picture of entanglement

(a) Interchain or intrachain transient coupling

Strong physical exchange takes place.

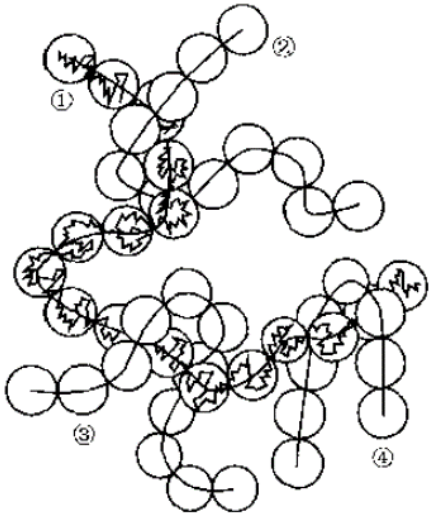
Polymer chain with polarity unit, e.g. transient network with metal ion complexation, etc. Non-universal

(b) and (c) Completely topological or purely geometric constraints



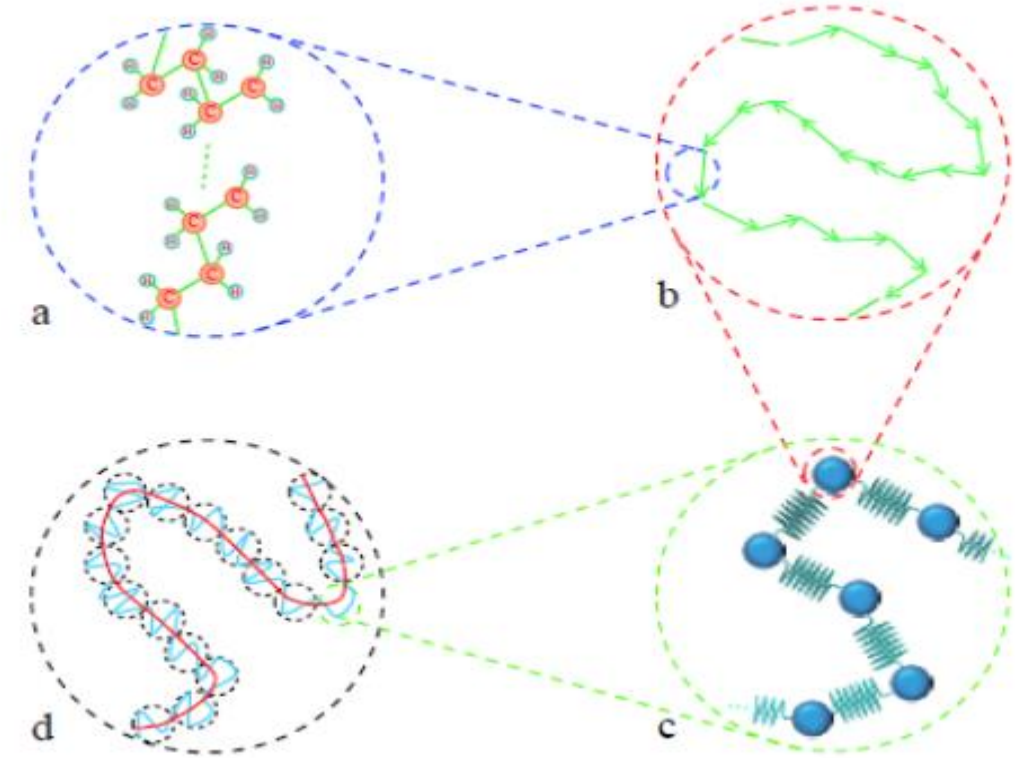
(b) Short-range entanglement: Very flexible linear polymer chain. knots or loops formed between chains. Non-universal

(c) Long-range entanglement(blob model): the chain within the blob do not penetrate to the inside of other chains. The entanglement can change and slide.



Coarse-grained model

How an unentangled or entangled polymer chains relax the anisotropy and related stress induced by a step strain?



Coarse-grained model of polymer chains at different length level:
(a) atomic chain, (b) kuhn chain, (c) bead-spring chain, (d) primitive chain

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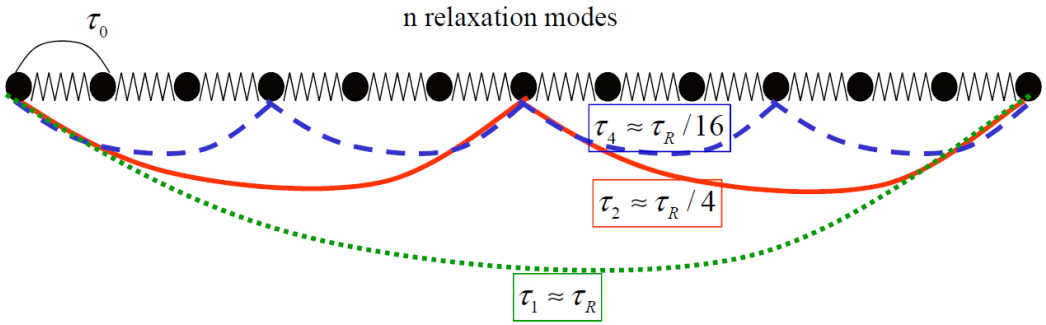
Rouse model for unentangled polymers



N beads of length b connected with N-1 springs

Relaxing a chain section of N/p monomers: $\tau_p \approx \tau_0 \left(\frac{N}{p}\right)^2$ (p = 1,2,3,…,N) $\tau_i < \tau_{i-1}$

The longest relaxation Rouse time: $\tau_R \approx \frac{R^2}{D_R} \approx \frac{R^2}{kT / N\zeta} = \frac{\zeta}{kT} NR^2$

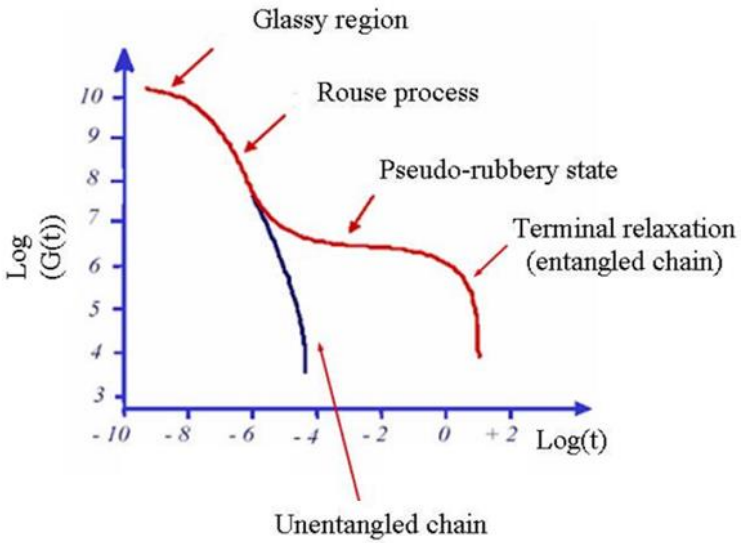
$t<t_R$: viscoelastic modes $t>t_R$: diffusive motion

Unentangled chain:

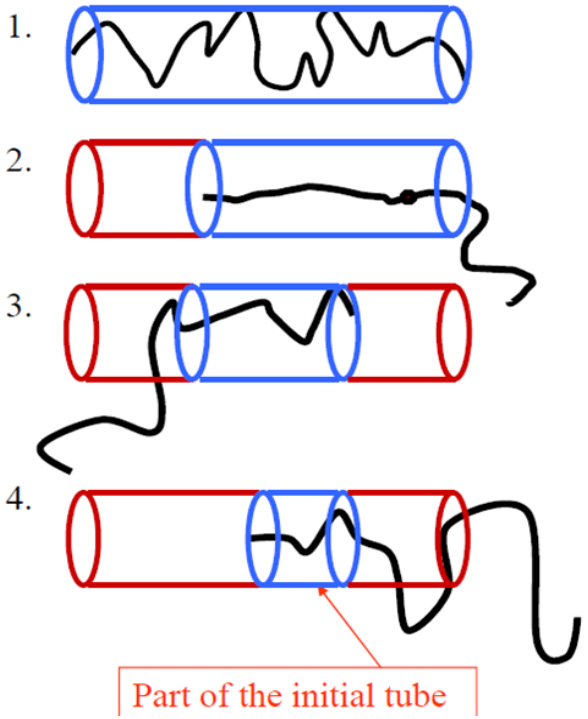
$$G(t) = \frac{\rho RT}{M} \sum_{p=1}^{N} \exp\left(\frac{-t}{\tau_p}\right) \quad \text{with} \quad \tau_p = \frac{\zeta_0 b^2 N^2}{6\pi^2 kTp^2}$$

Entangled chain:

$$G(t) = G_N^0 + G_{Rouse}(t) \approx G_N^0 + \frac{\rho RT}{M} \sum_{p=Z}^{N} \exp\left(\frac{-t}{\tau_p}\right)$$

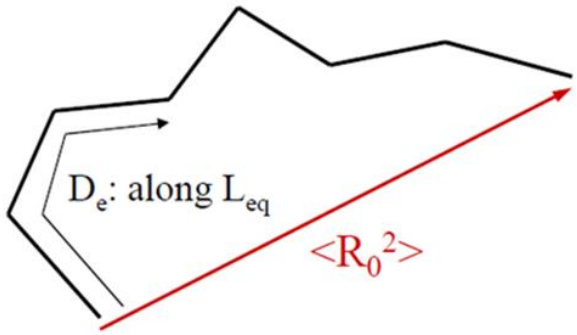


De Gennes-Reptation



1-D curvilinear diffusion

As the primitive chain diffuses out of the tube, a new tube is continuously and randomly being formed, starting from the ends.



curvilinear diffusion coefficient:

$$D_e = \frac{kT}{\zeta_{tot}} = \frac{kT}{N\zeta_0}$$

Total friction of the chain

Monomeric friction

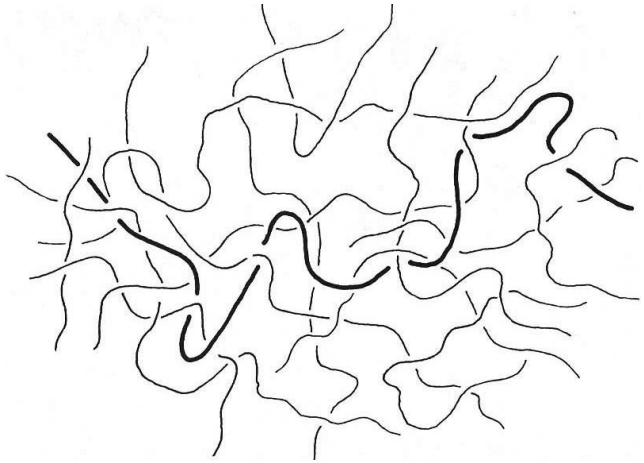
reptation time:

$$\tau_{rept} = \frac{L_{eq}^{\ 2}}{D_e} \propto \frac{N^2}{N^{-1}} = N^3$$

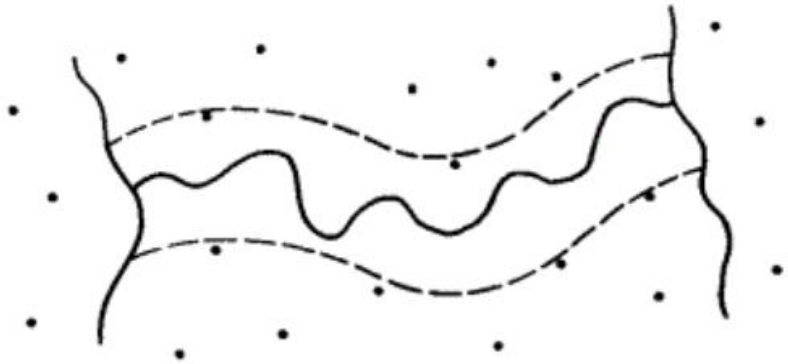
$$\tau_{Re\,pt} \approx \tau_e \left(\frac{N}{N_e}\right)^3$$

Doi-Edwards -Tube model

complex dynamics of inter-chain interaction



“single-body” problem



The assumptions of the tube model:

- The molecular environment of an observed chain is represented by a mean field called the “tube”, a fixed permanent network.
- Lateral motions are limited to a characteristic distance, the tube diameter. Only motions parallel to the curvilinear tube axis are unhindered, primitive length with a constant value.
- Based on the Reptation theory, the motion of the center of mass can go back and forth along the tube axis, and the advancing chain end can be randomly oriented.

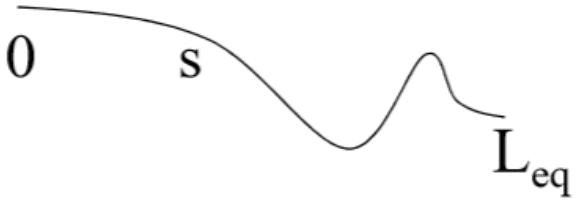
How much fraction of a chain can be relaxed or unrelaxed with time?

Assuming the equivalence between the diffusion of an entanglement segment along the tube and the diffusion of a tube segment along the chain, under the assumption of a Gaussian chain:

$$\frac{\partial\, p(s,t)}{\partial\, t} = D_e \cdot \frac{\partial^2 p(s,t)}{\partial\, s^2}$$

$$p(0,t) = p(L,t) = 0$$

$$p(x,0) = 1, \quad \forall x \in (0,L)$$



P(s,t): survival probability of an initial tube segment localized at a distance s at time t

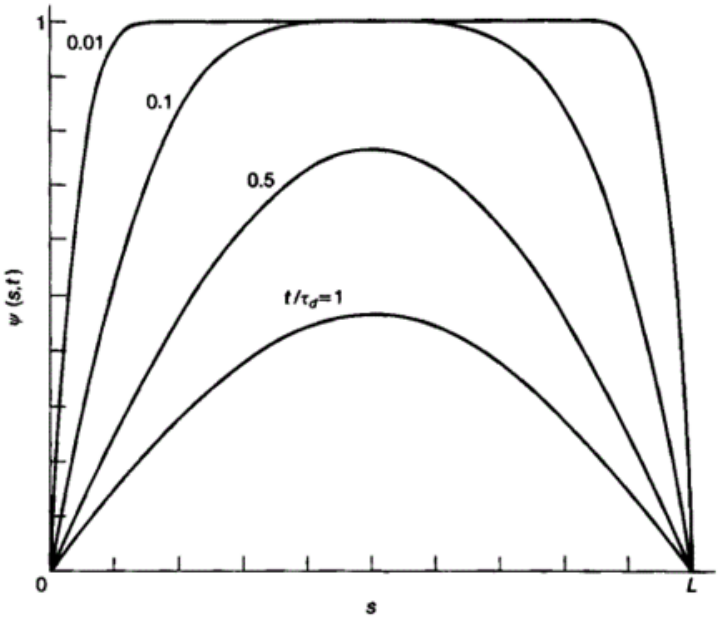
$$p(s,t) = \sum_{i\ odd} \frac{4}{p\pi} \cdot \sin\left(\frac{i\pi s}{L_{eq}}\right) \cdot \exp\left(\frac{-i^2\pi^2 D\ t}{L_{eq}^{\ 2}}\right)$$

- Unrelaxed fractions:

$$p_{rept}(t) = \int_0^L p(s,t)ds = \frac{8}{\pi^2} \sum_{i\ odd} \frac{1}{i^2} \exp\left(\frac{-i^2 D\ t}{L_{eq}^{\ 2}}\right)$$

- Relaxation modulus

$$G(t) = \frac{8}{\pi^2} G_N^0 \sum_{p\ odd} \frac{1}{p^2} \exp\left(\frac{-p^2 t}{\tau_{rept}(M)}\right)$$



Scaling from DE model:

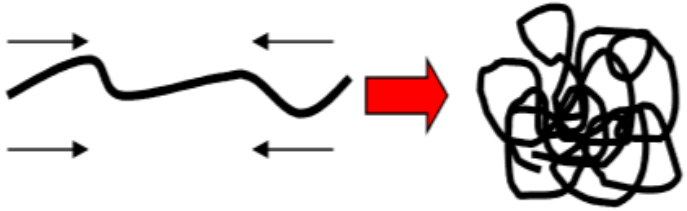
$\tau_{rept} \propto M^3$

$\eta_0 \propto G_N^0 . \tau_d$, $\eta_0 \propto M^3$

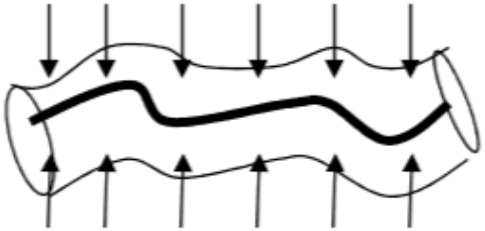
Scaling from experiment:

$\eta_0 \propto M^{\alpha}$ { $M>M_c$, $\alpha=1$; $M>M_c$, α close to 3.2-3.4

Entropic force



Topological force

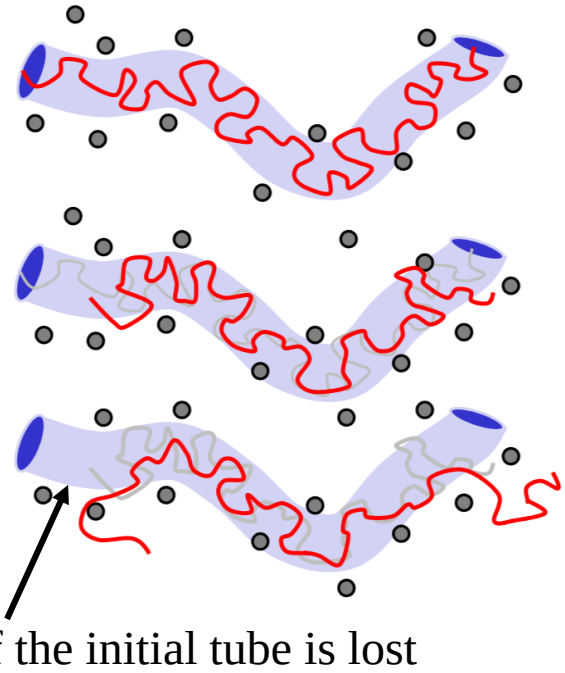


Equilibrium length is only the most probable length, representing the most stable configuration. Other chain lengths are possible, by thermal fluctuations around this equilibrium.

Additional relaxation mechanism?

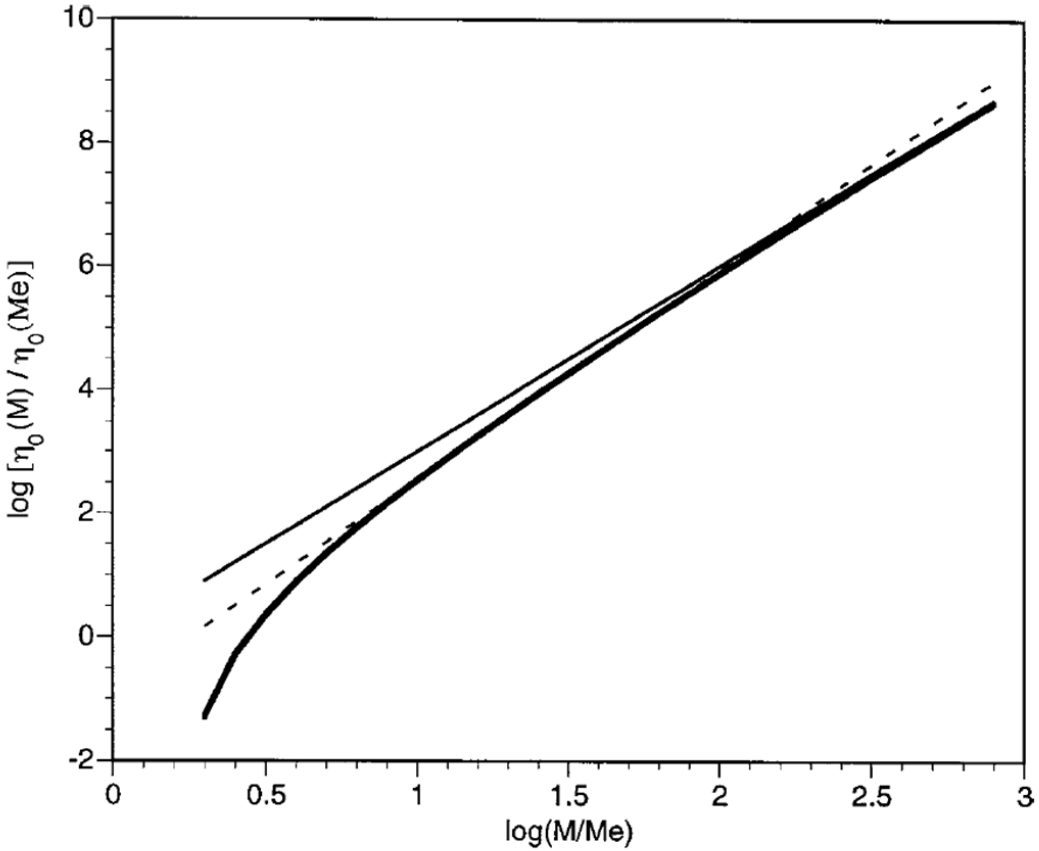
Contour Length Fluctuation (CLF)

CLF is a Rouse relaxation of the chain ends, the orientation of the ends of the initial tube is forgotten, which does not requires the motion of the center of mass, already described by Reptation.



- $\tau_e < t < \tau_{Rouse}$, CLF takes place
- At $t > \tau_{Rouse}$, Reptation process will start but in an effectively shortened tube length. CLF will speed up the overall relaxation of the polymer.

The scaling of the fraction of tube relaxed by CLF on Z is $Z^{-1/2}$, the importance of CLF becomes smaller as Z increases.



Prediction of the zero-shear viscosity η_0, normalized by the zero-shear viscosity of a polymer with molecular weight corresponding to one entanglement, as a function of normalized molecular weight $Z = M/M_e$ for pure reptation (solid thin line), reptation with fluctuations, given by Eq. 6.33 with $X = 1.3$ (solid thick line), and the empirical formula $\eta_0 \propto M^{3.4}$ (dashed line).

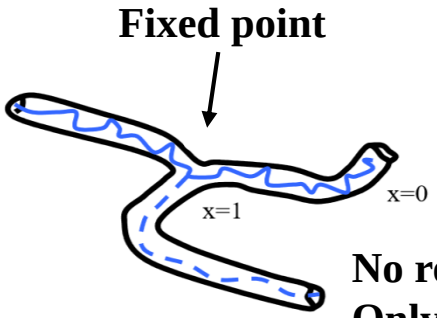
The solid thin line: pure reptation

The solid thick line: reptation with CLF

The dashed line: empirical formula,

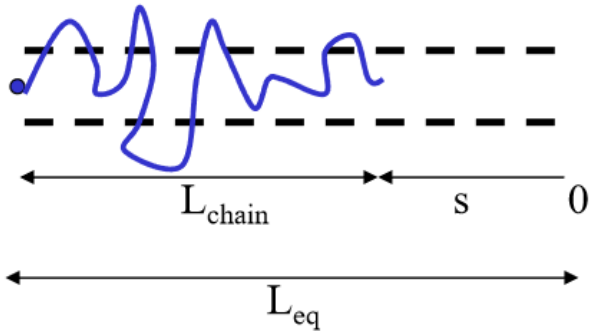
$$\eta_0 \propto M^{3.4}$$

Star polymers



No reptation
Only fluctuation

$$x = \frac{s}{L_{eq}}$$



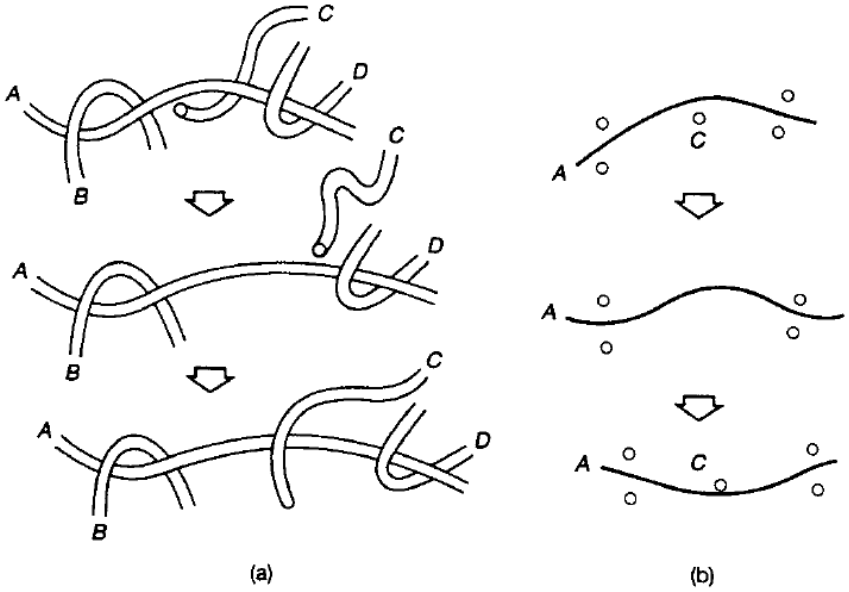
The potential retraction energy: $U(x) = \frac{3kT}{2} Z \cdot x^2 + const.$

- $U(x)<k_BT$, **the early fluctuation**: the chain easily fluctuates inside the tube without any topological constraints.
- $U(x)>k_BT$, **the activated fluctuations**: refers to retraction of the inner part of the chain which requires deep fluctuation to reach it due to topological constrains.

$$\tau_{CLF}(x) = \begin{cases} \tau_{early}(x) = \frac{9\pi^3}{16} \cdot \left(\frac{M_a}{M_{e,0}} \right)^2 \cdot \tau_{R,chain} \cdot x^4 & x < x_{trans} \\ \tau_{fluc}(x_i) = \tau_{early}(x_i) \exp\left(\frac{\Delta U(x_{trans,i} \rightarrow x_i)}{kT} \right) & x > x_{trans} \end{cases}$$

x_{trans} corresponds to the transition between these two mechanisms where $U(x_{trans})=k_BT$

Constraint Release (CR)

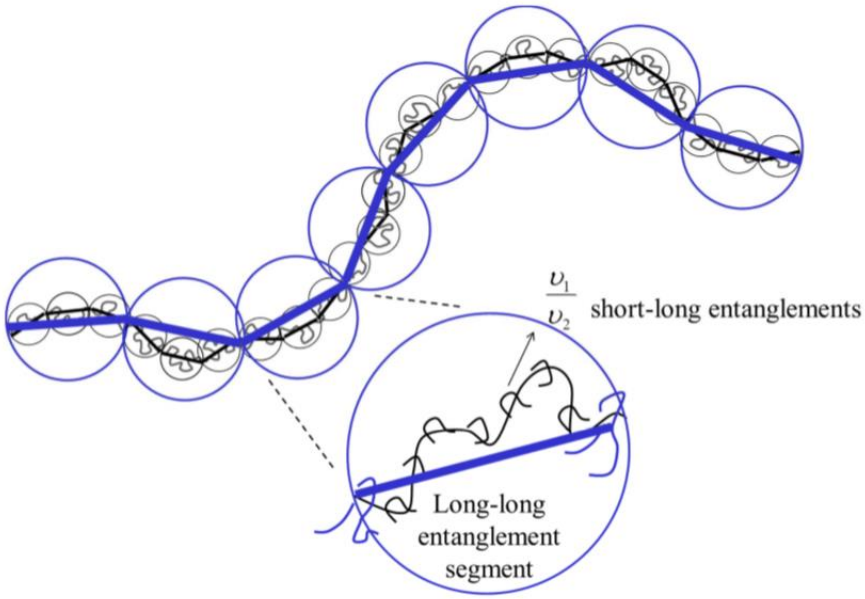


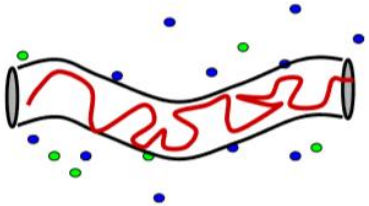
The tube motion is disregarded in the Doi and Edwards model, which is in particular important for bi- or poly- dispersed systems.

Tube motions chiefly affect the test chain in two different ways: slow motion and fast motion

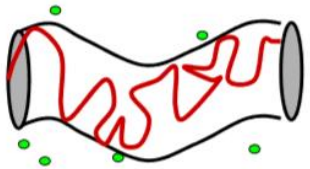
Fast motions of surrounding chains: the effect is equivalent to an increase of the "effective" tube diameter, which leads to an acceleration of the other relaxation processes (Reptation, CLF), and is called "Dynamic Tube Dilation".

Dynamic Tube Dilation





For t ≈0



After the relaxation of the blue chains

$$M_e(t) = \frac{M_{e,0}}{\Phi(t)^{\alpha}} \quad \begin{cases} L_{eq}(t) = L_{eq,0}\ \Phi(t)^{\alpha/2} \\ a(t) = \dfrac{a_0}{\Phi(t)^{\alpha/2}} \end{cases}$$

$$G(t) = \frac{\rho RT}{M_e(t)}\ \Phi(t) = \frac{\rho RT}{M_{e,0}}\ \Phi(t)^{\alpha+1}$$

The exponent α, called the dilution exponent takes a value between 1 and 1.3.

These "effective" values are different from the true material parameters (except at time zero) but the equilibrium values do not change. DTD affects the reptation dynamics: reptation time is proportional to $\Phi(t)^{\alpha}$.

What about if the tube dilates faster than the test chain is able to explore it?

Constraint release Rouse regime

- A small fraction of long chains is diluted in a matrix of short chains. The tube can be very wide, and even non-existent if the long chains are extremely diluted.

- A chain cannot explore the tube faster than the unconstrained Rouse process:

$$\Phi(t_i) > \Phi(t_{i-1})\left(\frac{t_{i-1}}{t_i}\right)^{\frac{1}{2}}$$

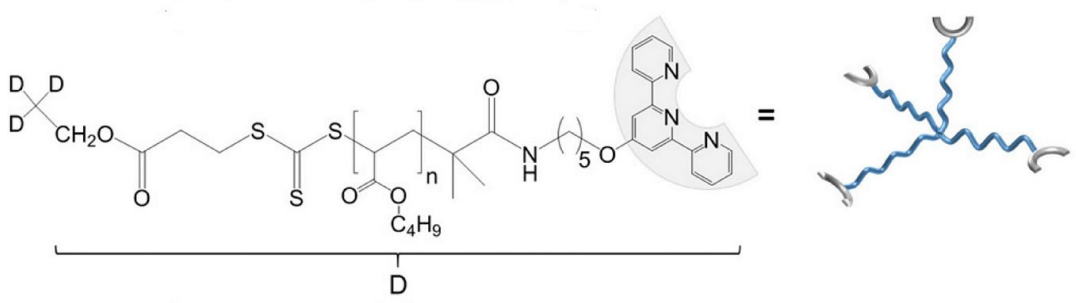
where $t_i - t_{i-1}$ is a small time increment during the relaxation process.

- The relaxation modulus $G(t) = G_N^0 \Phi(t)^\alpha \varphi(t) = \frac{\rho RT}{M_e(t)} \varphi(t)$

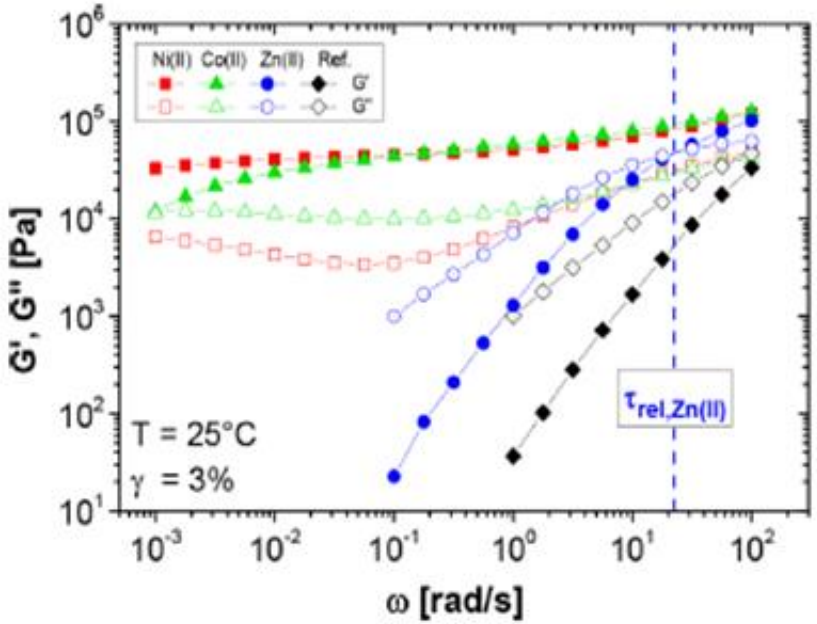
Where $\varphi(t)$ describes the segmental fraction which is still oriented (i.e. not relaxed by reptation or CLF) and Φ(t) is the "CRR limited" unrelaxed fraction.

Blend two metal-ligand crosslinks in telechelic star polymer

Materials



(a) Four-arm telechelic star PnBA-tpy4, M_n=249kg/mol



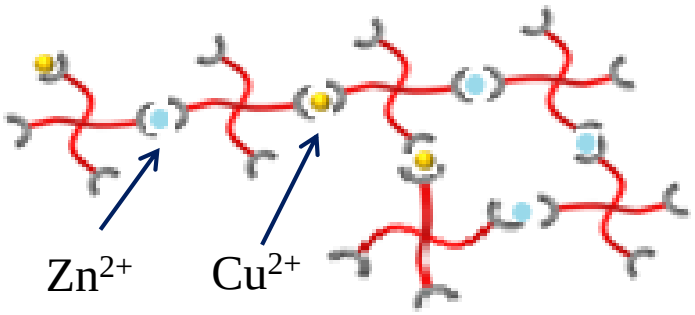
(b) Linear rheology curves at 25°C of four-arm star PnBA-tpy4 (melts) with different transition metal ions. The diamonds correspond to the reference polymer without metal ions. The storage modulus G' is represented by filled symbols and the loss modulus G'' by unfilled symbol.

relaxation time/stability: $Zn^{2+} < Cu^{2+} < Co^{2+} < Ni^{2+}$

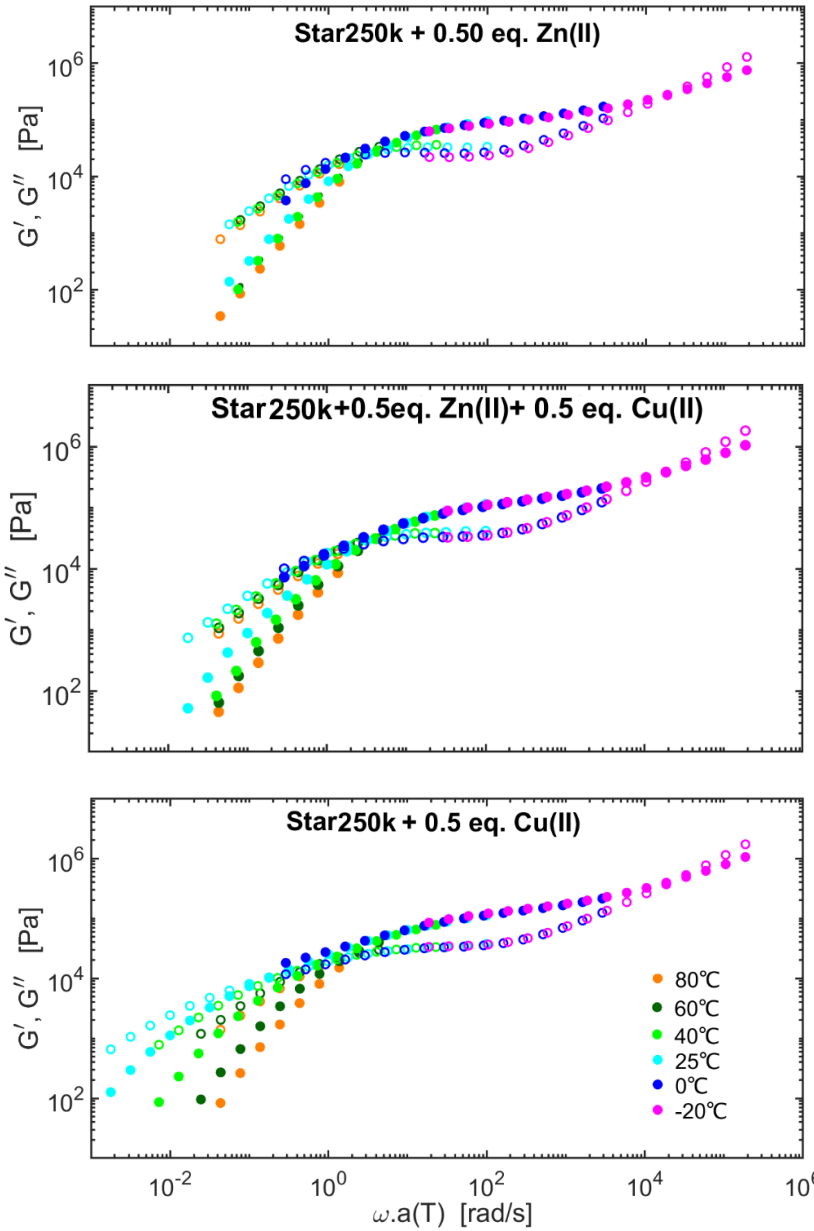
Macromolecules, 2017, 50, 5165−5175.

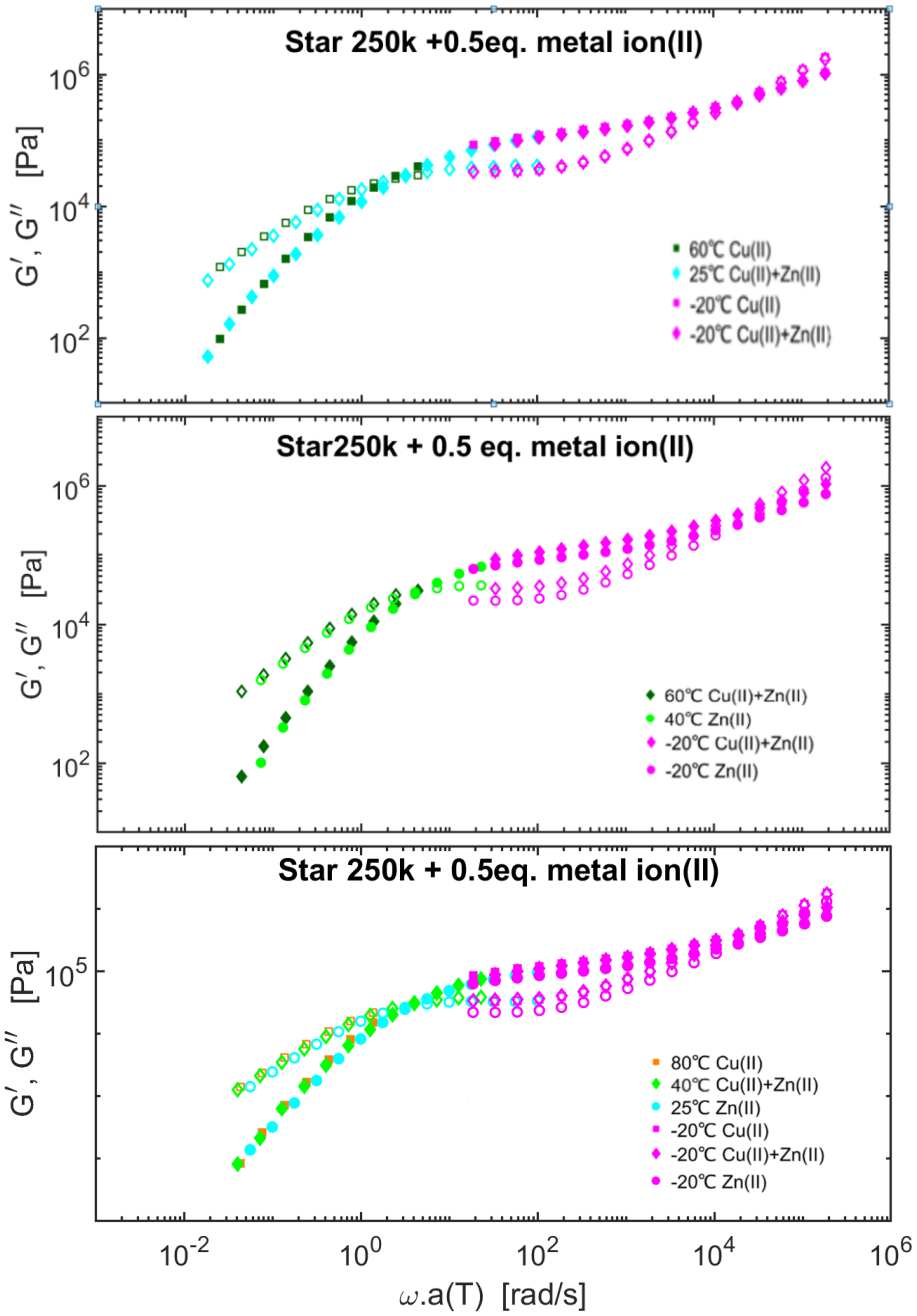
Experiment result

Stoichiometric amount (0.5eq. Cu^{2+} and 0.5eq. Zn^{2+}）



- Shift factor: taken from reference sample without metal ion. (reference temperature 25℃)
- The metal-ligand complex dependence on the temperature: Overall delay of the star relaxation
- The blends relaxation mechanism lies somewhere in between the single metal ions, but a little close to Zn^{2+}





Cu+Zn: 25°C

Cu: 60°C

Zn: 40°C

Cu+Zn: 60°C

Zn: 25°C

Cu+Zn: 40°C

Cu: 80°C

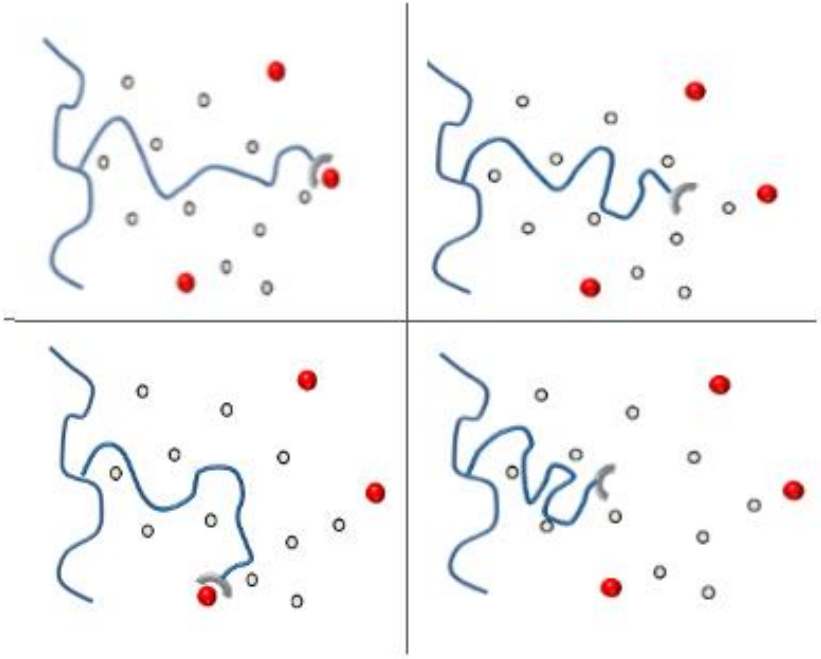
Elongation field?

Modelling

$$P(x,t)=\exp\left(\frac{-t}{\tau_{fluc}(x)}\right) \Rightarrow P(x,t)=\exp\left(\frac{-p_{free}\,t}{\tau_{fluc}(x)}\right)$$

p_{free}, average probability for a sticker to be free.

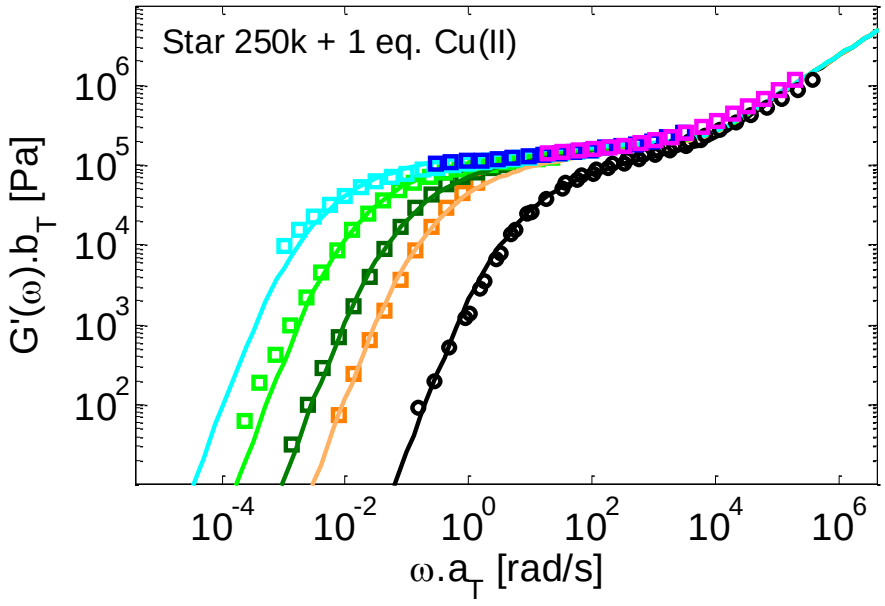
τ_{free}, the average time during which a dissociated end group will stay free before re-association.

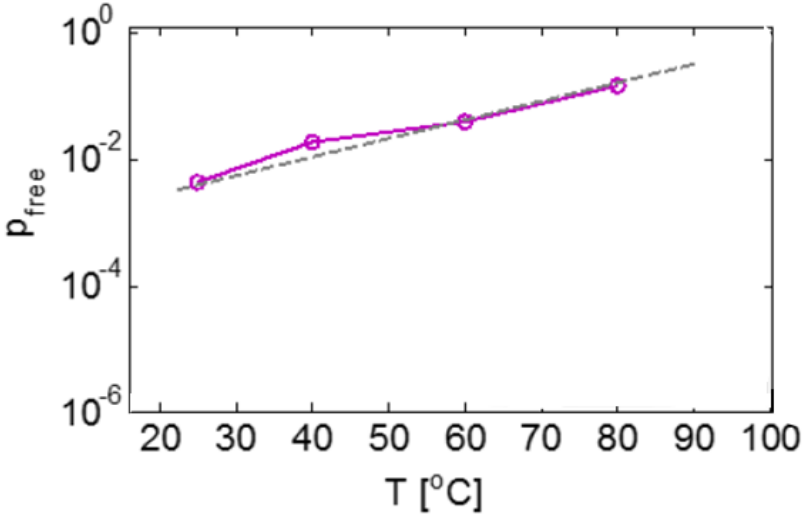


Depending on the ratio between the fluctuation time $\tau_{fluc\,(x)}$ and the free time, τ_{free}.

$\tau_{fluc\,(x)} < \tau_{free,}$ the chain can disentangle and relax its carrying stress in a single dissociation step.

$\tau_{fluc\,(x)} > \tau_{free}$, the relaxation by fluctuations of the deeper arm segments can require several dissociation/association events before taking place.





$$P(x,t)=\exp\left(\frac{-p_{free}\,t}{\tau_{fluc}(x)}\right)$$

several dissociation/association

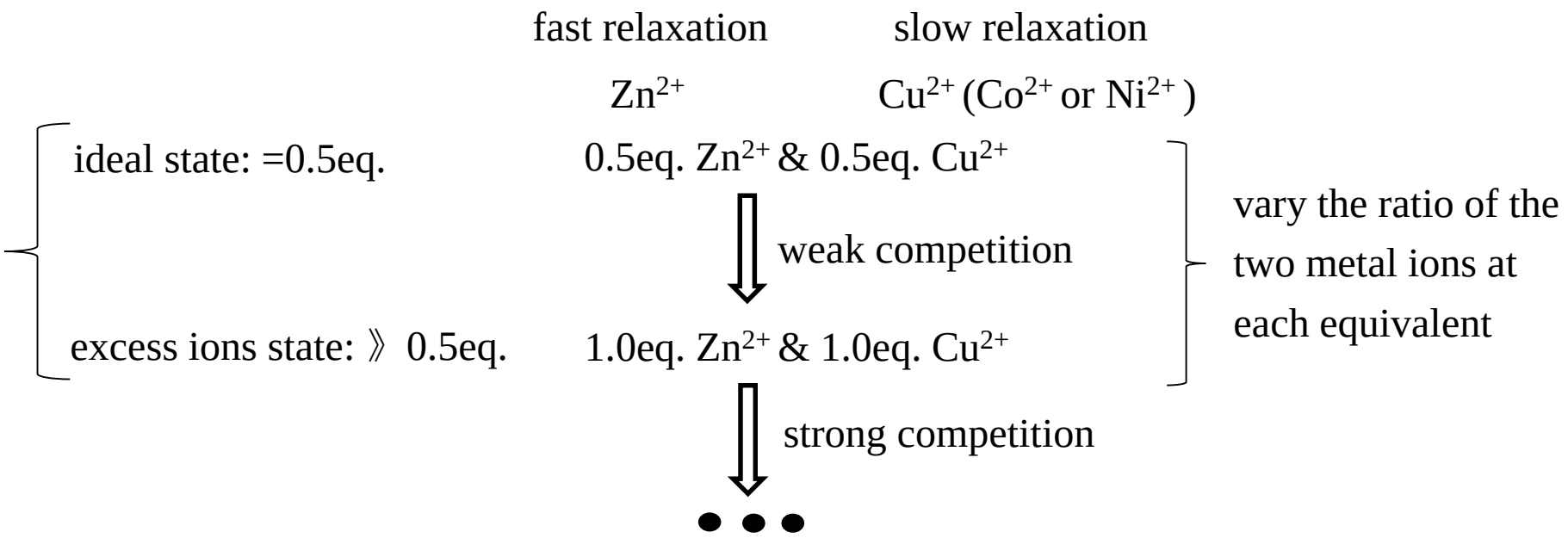
$$P(x,t)=\exp\left(\frac{-p_{free}\,t}{\tau_{total}(x)}\right)\ ??$$

The total time, $\tau_{total}(x)$, during which an arm must stay free in order to observe the relaxation of the arm segment x.

Perspectives

1. Modelling the data of the blend using the methods for single metal ions.

2. Studying different ratio of two metal ions(e.g. 0.25:0.75, etc) and excess state of the metal ions(e.g. 1eq. metal ions, etc.)



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Thank you for your attention!